Macropolyhedral Boron-containing Cluster Chemistry. A Reductive Trimerisation of MeNC to give an Imidazole-based Carbene stabilized by Coordination to Boron in an Eighteen-vertex Cluster Compound

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Reaction of MeNC with *anti*-$B_{18}H_{22}$ yields 7-{$(MeNH)C_3N_2HMe_2$}-*anti*-$B_{18}H_{20}$, in which a reductive trimerisation of MeNC *via* a cluster redox process gives an unusual imidazole-based carbene, {$(MeNH)C_3N_2HMe_2$}, that is stabilized by coordination to the {*anti*-B_{18}} macropolyhedral cluster.[1]

Although the basic chemistry of many boron-containing single-cluster compounds is receiving increasing attention, the potentially greater chemistry of the macropolyhedral boron-containing compounds, *i.e.* those with structures based on the fusion, with common edges or faces, of the basic single clusters, is hitherto essentially unexamined.[1–4] The best known macropolyhedral borane is eighteen-vertex *anti*-$B_{18}H_{22}$. Its structure is based on the fusion, with a common two-boron edge, of two ten-vertex *nido*-$B_{10}H_{14}$-type clusters.[5] During the course of the examination of the further chemistry of this compound, we have found an interesting reaction with methylisonitrile, MeNC, for which we now report preliminary findings.

Because of the high Brønsted acidity[6] of *anti*-$B_{18}H_{22}$, its reaction with many aprotic two-electron donors L results in simple salt generation to give $[LH]^+[anti\text{-}B_{18}H_{21}]^-$. By contrast, we have now found that with the weaker unsaturated ligand MeNC the interesting species 7-$[(MeHN)C_2N_2HMe_2]$-*anti*-$B_{18}H_{20}$ (compound **1**)† is formed. Thus reaction between an excess of MeNC and *anti*-$B_{18}H_{22}$ in benzene for 24 h at room temperature, followed by heating at reflux for 24 h, filtration, and then repeated separations of the soluble fraction by column chromatography (silica gel; CH_2Cl_2–MeCN 2:1 v/v), resulted in three main components. Recrystallisation from CH_2Cl_2–hexane (1:2 v/v) purified one of these {of analytical R_F 0.77, foil-backed silica G (Kavalier), CH_2Cl_2–MeCN 2:1 v/v} and permitted its identification as compound **1** (pale yellow crystals, 32%), by single-crystal X-ray diffraction analysis (Fig. 1) together with NMR spectroscopy and mass spectrometry.§

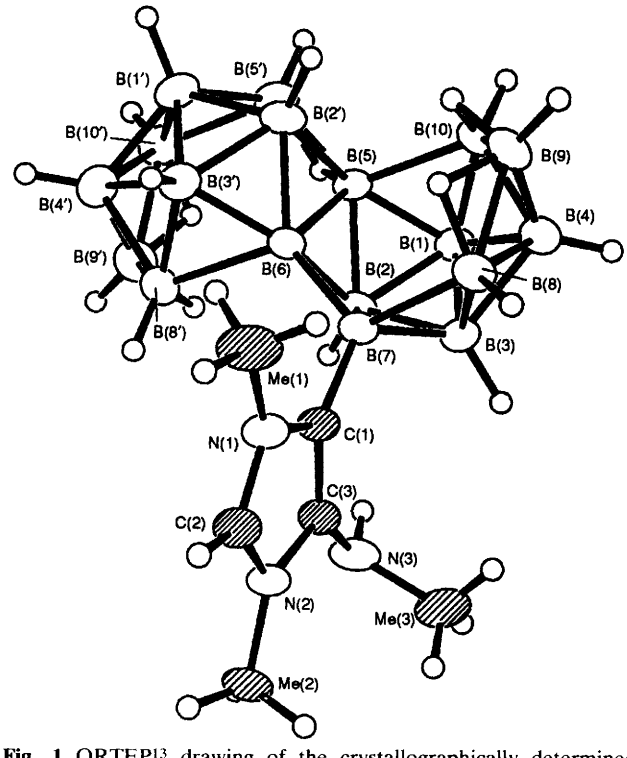


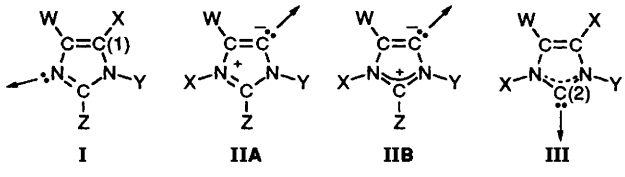
Fig. 1 ORTEP[13] drawing of the crystallographically determined molecular structure of 7-$[(MeNH)C_2N_2HMe_2]$-*anti*-$B_{18}H_{20}$ with numbering according to the *nido*-decaborano-[6′,7′:5,6]-*nido*-decaborane system (compare ref. 1). Selected distances (pm) and angles (°): C(1)–B(7) 1.576(2), C(1)–N(1) 1.402(2), N(1)–C(2) 1.326(2), C(2)–N(2) 1.326(2), N(2)–C(3) 1.388(2), C(3)–C(1) 1.369(2), N(1)–CMe(1) 1.462(2), N(2)–CMe(2) 1.466(2), C(3)–N(3) 1.392(2), B(6)–B(7) 1.682(2), B(7)–B(8) 1.864(2), B(5)–B(6) 1.788(2), B(5)–B(10) 2.003(3), B(6)–B(8′) 2.009(2), C(1)–N(1)–C(2) 110.46(12), N(1)–C(2)–N(2) 108.68(13), C(2)–N(2)–C(3) 108.09(12), N(2)–C(3)–C(1) 108.79(12), C(3)–N(3)–CMe(3) 115.30(13), B(3)–B(7)–C(1) 117.82(12), B(2)–B(7)–C(1) 122.65(11), B(6)–B(7)–C(1) 122.25(13), and B(8)–B(7)–C(1) 120.17(11).

The reaction appears to be a stoichiometric process [eqn. (1)] in which the macropolyhedral cluster oxidation is achieved by a rather unusual reductive oligomerisation of MeNC to give the *C*-methylamino- and *N,N′*-dimethyl-substituted imidazole-like ligand {$(MeNH)C_2N_2HMe_2$}. This {$(MeNH)C_2N_2HMe_2$} unit derives formally from the nitrogen-donor imidazole residue **I** by the transfer of the substituent from C(1) to generate an effective carbene ligand **IIA** which exhibits some delocalisation **IIB** and zwitterionic character. Both free and bound imidazole-based carbene ligands are rare,[7] and those that are known have the carbene centre at the carbon atom C(2) that is flanked by the two nitrogen atoms (schematic **III**). In compound **3** the carbene-to-boron donor linkage is weak at 169 pm, but the presence of a C–B linkage suggests a mechanism with an initial attack by the MeNC isonitrile carbon at B(7). The subsequent reductive trimerisation is of interest: although single, double, triple, and polymeric isonitrile insertions, principally into carbon–metal bonds, have long been known,[8] the products invariably have acyclic polycarbon backbones, rather than cyclised azacarbane ones as reported here. Preliminary investigation of the remaining chromatographic component mixtures from reaction (1) suggest other 7-$LB_{18}H_{20}$ species in which L derives from other reductive oligomerisations of the MeNC substrate. These are proving more difficult to purify, but we hope to report more fully on them, together with other aspects of the new chemistry, in the future.

anti-$B_{18}H_{22}$ + 3 MeNC → 7-$[(MeNH)C_2N_2HMe_2]$-*anti*-$B_{18}H_{20}$ (1)

syn-$B_{18}H_{22}$ + $C_6H_{11}NC$ → $(C_6H_{11}NH_2)CB_{18}H_{20}$ (2)

nido-$B_{10}H_{14}$ + 2 MeNC → 6,9-$(MeNC)_2$-*arachno*-$B_{10}H_{12}$ + H_2 (3)



This methylisonitrile reaction of *anti*-$B_{18}H_{22}$ [eqn. (1)] contrasts to that of the *syn*-$B_{18}H_{22}$ isomer† with cyclohexylisonitrile, which, interestingly, is reported to result in carbon-vertex insertion to give a monocarbaborane formulated as a nineteen-vertex cluster compound $(C_6H_{11}NH_2)CB_{18}H_{20}$ [eqn. (2)].[2] It also contrasts to the behaviour of the single-cluster model compound *nido*-$B_{10}H_{14}$, which exhibits a very facile and well-studied reaction with two-electron ligands such as MeNC to give bis(ligand) *arachno* species 6,9-$L_2B_{10}H_{12}$ [*e.g.* eqn. (3)].[9] These contrasts in reaction behaviour are quite marked, and other related reactions, either with the two $B_{18}H_{22}$ isomers or with other macropolyhedral boron-containing compounds, should generate further interesting new compounds with novel structural features and other properties, and we are currently exploring some of these possibilities.[10]

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Footnotes

† *Nomenclature*: The IUPAC-recommended nomenclature for *anti*-$B_{18}H_{22}$ (also known as *n*-$B_{18}H_{22}$, see ref. 1) is *nido*-decaborano-[6′,7′ : 5,6]-*nido*-decaborane. In this nomenclature the ligand derivative described here has the formulation 7-ligand-*nido*-decaborano-[6′,7′ : 5,6]-*nido*-decaborane; it is enantiomeric, the other enantiomer being formally 5-ligand-*nido*-decaborano-[5′,6′ : 6,7]-*nido*-decaborane. The compound *syn*-$B_{18}H_{22}$ (also known as *iso*-$B_{18}H_{22}$) consists of the *nido*-decaborano-[5′,6′ : 5,6]- and -[6′,7′ : 6,7]-*nido*-decaborane enantiomeric pair.

‡ *Crystallography*: All measurements were made at 200 K on a Stoe STADI4 diffractometer operating in the ω-θ scan mode using graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). The structure was determined by direct methods using the SHELXS-86 program,[11] and was refined by full-matrix least-squares analysis (based on F^2) using SHELXL-93.[12] All non-hydrogen atoms were refined with anisotropic displacement parameters. The methyl hydrogen atoms were placed in calculated positions (C–H = 0.98 Å) and refined with a fixed isotropic displacement parameter of 1.5 U_{eq} of the parent carbon atom; all other hydrogen atoms were located on a Fourier difference map and were freely refined. The weighting scheme $w = [\sigma^2(F_o^2) + 0.0572(P)^2 + 0.2230P]^{-1}$ was used, where $P = (F_o^2 + 2F_c^2)/3$.

Crystal data: $C_6H_{31}B_{18}N_3$, M_r = 339.92, space group $P\bar{1}$, triclinic, a = 8.9958(5), b = 10.6760(6), c = 11.0346(8) Å, α = 88.548(5), β = 84.979(5), γ = 77.641(4)°, U = 1.9453(4) nm³, Z = 2, D_c = 1.095 g cm^{-3}, μ = 0.354 mm^{-1}, $F(000)$ = 356. All 3403 unique data collected in the range $3.0 < 2\theta < 50°$ were used in refinement which converged with R_1 { = $\Sigma||F_o| - |F_c|| / \Sigma|F_o|$} = 0.0404 and wR_2 { = $(\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2])^{\frac{1}{2}}$} = 0.1125. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at The Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ *NMR and mass spectrometry*: NMR data for compound **1** as follows {as: assignment δ(^{11}B) [δ(^{1}H) in square brackets]} for $(CD_3)_2CO_2$ solution at 294–303 K: ligand-substituted decaborane subcluster: BH(1) −12.0 {+1.90 or +2.20], BH(2) −24.2 [−0.01], BH(3) +5.5 [+3.21], BH(4) −41.6 [+0.32], BH(7) −5.1 [ligand position], BH(8) −12.0 [+2.20 or +1.90], BH(9) −7.6 [+2.65], BH(10) +4.1 [+3.65]; unsubstituted decaborane subcluster: BH(1′) +13.5 [+3.55], BH(2′) −29.5 [−0.83], BH(3′) −3.4 [+2.72], BH(4′) −38.9 [+0.19], BH(5′) −12.0 [+2.80], BH(8′) +8.3 [+3.20], BH(9′) −0.2 [+2.90], BH(10′) −9.2 [+2.55]; common atoms: B(5/6′) −0.20 [–], B(6/7′) +15.3 [–]; bridging H atoms: μ-H(8,9) −3.60, μ-H(9,10) −1.38, μ-H(5′, 5/6′) −1.80, μ-H(8′,9′) −1.23, μ-H(9′,10′) −2.92; NMR assignments by [^{11}B–^{11}B]-COSY experiments and ^{1}H-{^{11}B(selective)} spectroscopy. Additional δ(^{1}H) data: MeNH +2.12 (3H, d, 5.9 Hz) and +1.68 (1H); Me +4.04 (3H) and +3.87 (3H); CH at +3.84 (1H, m). These data are very similar to those for the isoelectronic and isostructural unsubstituted analogue, the [*anti*-$B_{18}H_{21}$]$^-$ anion (ref. 1), which can be regarded for comparison as a 7-L-*anti*-$B_{18}H_{20}$ species where L is the two-electron donor H^-. Mass spectrometry (70 eV EI ionisation) gave m/z_{max} 343 corresponding to the highest isotopomer of the proposed molecular ion.

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